

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C03C 23/00, B08B 9/00, 3/00, 3/14, 7/00		A1	(11) International Publication Number: WO 00/68159
			(43) International Publication Date: 16 November 2000 (16.11.00)
<p>(21) International Application Number: PCT/US00/11271</p> <p>(22) International Filing Date: 27 April 2000 (27.04.00)</p> <p>(30) Priority Data: 09/305,971 6 May 1999 (06.05.99) US</p> <p>(63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 09/305,971 (CON) Filed on 6 May 1999 (06.05.99)</p> <p>(71) Applicant (for all designated States except US): PHILLIPS PETROLEUM COMPANY [US/US]; 4th and Keeler, Bartlesville, OK 74004 (US).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): GEIBEL, Jon, F. [US/US]; 2600 Mountain Road, Bartlesville, OK 74003 (US). GREEN, Richard, A. [US/US]; 631 SE Wilshire Ave, Bartlesville, OK 74006-8427 (US).</p> <p>(74) Agents: RICHARDS, John; Ladas & Parry, 26 West 61st Street, New York, NY 10023 (US) et al.</p>			<p>(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>
<p>(54) Title: PROCESS TO REMOVE POLY(ARYLENE SULFIDE) BASED DEPOSITS FROM AN ARTICLE</p> <p>(57) Abstract</p> <p>A process for the removal of poly(arylene sulfide) based deposits from an article by contacting said poly(arylene sulfide) based deposits with a polar aprotic compound, a base, an organosulfur compound having the formula: R₁-S-S-R₂, wherein R₁ and R₂ are hydrocarbon radicals having from 1 to 50 carbon atoms per radical, and optionally, a halogenated aromatic compound.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

PROCESS TO REMOVE POLY(ARYLENE SULFIDE)
BASED DEPOSITS FROM AN ARTICLE

Field of the Invention

This invention relates to a process for removing poly(arylene sulfide)
5 based deposits from an article.

Background of the Invention

In the production of poly(arylene sulfide) polymers, poly(arylene
sulfide) based deposits can form on surfaces of production equipment. In addition,
a batch of poly(arylene sulfide) polymer can gel in a reactor and have to be
10 removed. Poly(arylene sulfide) based deposits can also form during subsequent
processing of the poly(arylene sulfide) polymer, such as in synthetic fiber
production. Machine parts utilized in processing the poly(arylene sulfide) polymer
which have poly(arylene sulfide) based deposits must be cleaned for re-use. Such
parts include, but are not limited to, spinnerettes, dies, pack parts, and filters.

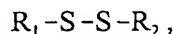
15 These poly(arylene sulfide) based deposits can be removed
mechanically, but the job is tedious and time consuming. Also, attempts to remove
the poly(arylene sulfide) based deposits by "burn out" procedures have been made.
For example, metal parts can be placed in a furnace to remove poly(arylene sulfide)
based deposits. However, this "burn out" procedure is not suitable for removing
20 poly(arylene sulfide) based deposits from all metal parts since the burn out can
cause corrosion, warping, or other problems.

There is a need in the poly(arylene sulfide) industry for an efficient
process to remove poly(arylene sulfide) based deposits from articles. This invention
provides such a process.

25 Summary of the Invention

The invention provides a process for removing poly(arylene sulfide)
based deposits from an article.

In accordance with this invention, a process for removing
poly(arylene sulfide) based deposits is provided, said process comprising contacting
30 said poly(arylene sulfide) based deposits with a polar aprotic compound, a base, an
organosulfur compound having the formula:

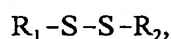


- 2 -

where R_1 and R_2 can be the same or different and are selected from the group consisting of hydrocarbon radicals having from 1 to 50 carbon atoms per radical, and optionally, a halogenated aromatic compound.

Detailed Description of the Invention

5 In this invention, a process is provided for removing poly(arylene sulfide) based deposits from an article said process comprising contacting said poly(arylene sulfide) based deposits with a polar aprotic compound, a base, an organosulfur compound having the formula:



10 where R_1 and R_2 can be the the same or different and are selected from the group consisting of hydrocarbon radicals having from 1 to 50 carbon atoms per radical, and optionally, a halogenated aromatic compound.

Poly(arylene sulfide) based deposits comprise poly(arylene sulfide) polymers. Poly(arylene sulfide) polymers can be prepared by any means known in the art. Generally, poly(arylene sulfide) polymers are prepared by reacting
15 components comprising a polyhalo-substituted cyclic compound and an alkali metal sulfide in a polar organic compound. The poly(arylene sulfide) polymers which are preferred for use in this invention, because of their frequent occurrence in polymer production and processing, are those polymers which consist essentially of repeating
20 units containing phenyl groups linked to one or more constituents selected from the group consisting of sulfur, oxygen, a ketone group, a biphenyl group, a sulfone group, and substituted and unsubstituted methyl groups. By use of the term "consist essentially of" it is intended that the poly(arylene sulfide) polymers do not contain any repeat unit which would have an adverse effect on the desired object of the
25 invention. Most frequently, the poly(arylene sulfide) polymer is poly(phenylene sulfide) due to its widespread use in the industry. Said poly(arylene sulfide) based deposits can further comprise other contaminants, such as, but not limited to, metal sulfides, oxides and other salts.

Said article can be any type of manufacture including, but not limited
30 to, process equipment, such as, reactor vessels, and subsequent processing equipment, such as, spinnerettes, dies, pack parts, and filters.

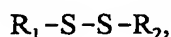
Said polar aprotic compound functions to provide a medium for

- 3 -

contacting said base and said organo-sulfur compound. Said polar aprotic compound includes, but are not limited to, cyclic or acyclic organic amides having from 1 to about 10 carbon atoms per molecule. Exemplary polar aprotic compounds are selected from the group consisting of 1,3-dimethyl-2-
5 imidazolidinone, formamide, acetamide, N-methylformamide, N,N-dimethylformamide, N,N-dimethylacetamide, N-ethylpropionamide, N,N-dipropylbutyramide, 2-pyrrolidone, N-methyl-2-pyrrolidone (NMP), ϵ -caprolactam, N-methyl- ϵ -caprolactam, N,N'-ethylenedi-2-pyrrolidone, hexamethylphosphoramide, tetramethylurea, and mixtures thereof. The preferred polar aprotic compound is
10 NMP due to its availability and ease of use.

Suitable bases for use in this invention are those strong enough to remove a proton from thiophenol. For example, said bases include, but are not limited to, sodium carbonate and alkali metal hydroxides selected from the group consisting of lithium hydroxide, sodium hydroxide, potassium hydroxide, rubidium
15 hydroxide, cesium hydroxide, and mixtures thereof. The preferred base is sodium carbonate due to availability and ease of use.

Said organosulfur compound includes compounds having the formula:



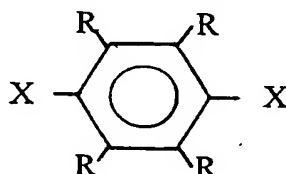
where R_1 and R_2 can be the same or different and are selected from the group
20 consisting of hydrogen and hydrocarbon radicals having from 1 to about 50 carbon atoms per radical. Preferably, said hydrocarbon radicals are selected from the group consisting of hydrogen and hydrocarbon radicals having from about 6 to about 24 carbon atoms. Most preferably, said hydrocarbon radicals are phenyl groups thus forming the compound, phenyl disulfide. Phenyl disulfide is highly efficient in
25 removing said poly(arylene sulfide) based deposits.

The polar aprotic compound, base, organosulfur compound, and article are contacted at a sufficient temperature and for a sufficient contact time to remove said poly(arylene sulfide) based deposit. Preferably, said temperature should be in a range of about 150°C to about 450°C. Temperatures below about
30 150°C may not cause removal of the poly(arylene sulfide) based deposits. Temperatures above 450°C can cause unnecessary side reactions to occur. Most preferably, said temperature should be in a range of 200°C to 280°C. Contact time

- 4 -

varies and can depend on the amount of deposits to be removed, and the concentration of the organosulfur compound, base, and polar aprotic compound utilized.

Suitable halogenated aromatic compounds can be represented by the
5 formula:



10 wherein X is a halogen, and R is selected from the group consisting of hydrogen, a halogen, alkyl, cycloalkyl, aryl, alkylaryl, and arylalkyl radicals having from about 6 to about 24 carbon atoms. Exemplary halogenated aromatic compounds include, but are not limited to, and are selected from the group consisting of *p*-dichlorobenzene, *p*-dibromobenzene, *p*-diiodobenzene, 1-chloro-4-bromobenzene, 1-
15 chloro-4-iodobenzene, 1-bromo-4-iodobenzene, 2,5-dichlorotoluene, 2,5-dichloro-*p*-xylene, 1-ethyl-4-isopropyl-2,5-dibromobenzene, 1,2,4,5-tetramethyl-3,6-dichlorobenzene, 1-butyl-4-cyclohexyl-2,5-dibromobenzene, 1-hexyl-3-dodecyl-2,5-dichlorobenzene, 1-octadecyl-2,5-diiodobenzene, 1-phenyl-2-chloro-5-bromobenzene, 1-*p*-tolyl-2,5-dibromobenzene, 1-benzyl-2,5-dichlorobenzene, 1-octyl-5-(3-
20 methylcyclopentyl)-2,5-dichlorobenzene, and mixtures thereof. The preferred halogenated aromatic compound for use in this invention is *p*-dichlorobenzene, hereinafter referred to as DCB, due to availability and ease of use.

EXAMPLE

The following example is intended to be illustrative of the invention
25 but is not meant to be construed as limiting the reasonable scope of the invention.

Example 1

The purpose of this example is to demonstrate that phenyl disulfide can be utilized to remove poly(phenylene sulfide), hereinafter referred to as "PPS", from a PPS molded part containing glass fibers.

30 To a 1 liter autoclave reactor, 0.0544 moles of sodium carbonate, 0.02723 moles of phenyl disulfide, and 3.00 moles of NMP were added. Then, a PPS molded part weighing 4.21 grams was placed in the reactor. The PPS molded

- 5 -

part contained 40% by weight glass fiber.

Oxygen was removed from the reactor utilizing 5 pressure and release cycles of 50 psig nitrogen and 5 pressure and release cycles using 200 psig nitrogen. 40 psig of nitrogen pressure was then maintained in the reactor. The reactor was
5 heated rapidly to 250°C and held for 2 hours. Then, the reactor was cooled rapidly to room temperature. The reactor was opened, and a mixture was removed from the reactor using a vacuum flask attached to a vacuum pump by polyethylene tubing. Additional NMP was used to remove the mixture from the reactor. The mixture was filtered through a Buchner funnel with Fisher brand P8 filter paper. After
10 essentially all of the liquid was filtered through the Buchner funnel, the solids were collected on the filter paper. The solids were removed from the filter paper by washing the solids several times with acetone and collecting the solids in another Buchner funnel containing filter paper. The solids were dried and then weighed. The solids weighed 5.03 grams. The solids were then washed with water several
15 times and dried in a vacuum oven at 100°C to produce water-washed solids. The weight of the water-washed solids was 1.41 grams.

These water-washed solids represented the glass fibers contained in the PPS molded part. 0.27 grams of the glass fibers were not recovered due to handling losses during the experiment. The PPS had been removed from the PPS
20 molded part by contacting the PPS molded part with phenyl disulfide, sodium carbonate, and NMP.

CLAIMS

1. A process for the removal of poly(arylene sulfide) based deposits from an article, said process comprising contacting said poly(arylene sulfide) based deposits with a polar aprotic compound, a base, and an organosulfur compound
5 having the formula:
- $$R_1-S-S-R_2,$$
- wherein R_1 and R_2 are hydrocarbon radicals having from 1 to 50 carbon atoms per radical, and optionally, a halogenated aromatic compound.
2. A process according to claim 1, wherein said poly(arylene sulfide)
10 based deposits are poly(arylene sulfide) polymers consisting essentially of repeating units containing phenyl groups linked to one or more constituents which are sulfur, oxygen, a ketone group, a biphenyl group, a sulfone group, or a substituted or an unsubstituted methyl group.
3. A process according to claim 1, wherein said polar aprotic compound
15 includes a cyclic or an acyclic organic amide having from 1 to about 10 carbon atoms per molecule.
4. A process according to claim 3, wherein said polar aprotic compound is 1,3-dimethyl-2-imidazolidinone, formamide, acetamide, N-methylformamide, N,N-dimethylformamide, N,N-dimethylacetamide, N-ethylpropionamide, N,N-dipropylbutyramide, 2-pyrrolidone, N-methyl-2-pyrrolidone, ϵ -caprolactam, N-methyl- ϵ -caprolactam, N,N'-ethylenedi-2-pyrrolidone, hexamethylphosphoramide, tetramethylurea, and mixtures thereof.
5. A process according to claim 4, wherein said polar aprotic compound is N-methyl-2-pyrrolidone.
- 25 6. A process according to claim 1, wherein said base includes sodium carbonate or an alkali metal hydroxide which is lithium hydroxide, sodium hydroxide, potassium hydroxide, rubidium hydroxide, cesium hydroxide, or a mixture of any two or more of said alkali metal hydroxides.
7. A process according to claim 6, wherein said base is sodium
30 carbonate.
8. A process according to claim 1, wherein said hydrocarbon radicals in said organosulfur compound are hydrogen or a hydrocarbon radical having from

about 6 to about 24 carbon atoms.

9. A process according to claim 8, wherein said organosulfur compound is phenyl disulfide.

10. A process according to claim 1, wherein said halogenated aromatic compound *p*-dichlorobenzene, *p*-dibromobenzene, *p*-diiodobenzene, 1-chloro-4-bromobenzene, 1-chloro-4-iodobenzene, 1-bromo-4-iodobenzene, 2,5-dichlorotoluene, 2,5-dichloro-*p*-xylene, 1-ethyl-4-isopropyl-2,5-dibromobenzene, 1,2,4,5-tetramethyl-3,6-dichlorobenzene, 1-butyl-4-cyclohexyl-2,5-dibromobenzene, 1-hexyl-3-dodecyl-2,5-dichlorobenzene, 1-octadecyl-2,5-diiodobenzene, 1-phenyl-2-chloro-5-bromobenzene, 1-*p*-tolyl-2,5-dibromobenzene, 1-benzyl-2,5-dichlorobenzene, 1-octyl-5-(3-methylcyclopentyl)-2,5-dichlorobenzene, or a mixture of any two or more of said halogenated aromatic compounds.

11. A process according to claim 10, wherein said halogenated aromatic compound is *p*-dichlorobenzene.

12. A process according to any one of the preceding claims wherein said contacting carried out at a temperature in the range of about 150°C to about 450°C.

13. A process for the removal of poly(arylene sulfide) based deposits from an article substantially as herein described.

14. A process for the removal of poly(arylene sulfide) based deposits from an article substantially as herein described with reference to the Example.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/11271

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C03C 23/00; B08B 9/00, 3/00, 3/14, 7/00

US CL : 134/2, 22.19, 36, 42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 134/2, 22.19, 36, 42

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,334,701A (ASH et al) 02 August, 1994, see abstract.	1
A	US 4,874,635 A (KARAS et al) 17 October 1989, see abstract.	1
A	US 4,988,796 A (CLIFFTON et al) 29 January 1991, see abstract.	1
A	US 5,245,000 A (BOBSEIN et al) 14 September 1993, see Abstract.	1



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

20 JUNE 2000

Date of mailing of the international search report

27 JUL 2000

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

SHARIDAN CARRILLO

Telephone No. (703) 308-0661